SYNTHESIS AND CHARACTERIZATION OF THIN FILMS FOR GAS SENSING

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1. Introduction

Rapid rise of industrialization and urbanization have caused critical air pollution. Air pollution is an indicator of environmental changes that impact health and human being. It also affects plants and materials and has been attributed to emissions from industries, vehicles, and kitchens and waste decay besides the emission from natural sources viz., soil erosion, sea spray, forest fire, volcanoes etc. Air pollution causes global warming, climate change and affects human being and environment directly and indirectly (Le et al., 2014; Kumar and Kumari, 2015; Ju et al., 2015; Gupta et al., 2017; 2019). Various environmental pollutants have foul odour. The main cause of odour pollution is animal rearing, landfills, sewage, treatment plants, oil palm, rubber mills, factories and dumpsites. Polluting gases get released in the atmosphere from leakage also. Many polluting gases exist in our environment are gases carbon monoxide (CO), carbon dioxide (CO_2), oxides of nitrogen (NOx: NO_2, NO), ammonia (NH_3), hydrogen sulfide (H_2S), sulphur dioxide (SO_2), Volatile organic carbons (VOCs) etc. (Najjar, 2011). The leakages of explosive and flammable gases are extremely dangerous for human beings and their belongings (Hubert et al., 2011). Hence, sensing of polluting gases are essentials and there is urgent need of development of low cost sensor.

Odour is of environmental concern and a personal sense of smell allows the people to detect the presence of some chemicals in the ambient air (Dalton, 2003; Héroux et al., 2004). It is a mixture of light and tiny molecules and is formed due to the presence of volatile organic compounds, sulphides of hydrogen, ammonia etc. present in any substance. Odorant particles are typically small, partly hydrophobic volatile organic molecules (Carven et al., 1996). Odour from foodstuffs, beverages and the odour of perfumes are not due to single molecular varieties but are the results of multiple mixtures of thousands of separate compounds. Odour is the result of the mixed influence of the mixture. The detection of odour is important to check quality of food and beverages or illness (Peris and Gilabert, 2009). Real time monitoring of odour, volatile organic compounds, harmful gases etc. are crucial to maintain human health and safety. Even at the low concentration, these pollutants can cause harmful effects. Flammable, explosive and toxic volatile organic gases can cause eyes and skin irritation, dyspnea, headache, nausea, and even death (Schiffman, 1998; Liu et al., 2012; Ju et al., 2015). The detection, monitoring and characterization of odour and odour causing pollutants are required for

environmental safety and wellbeing of human. Gas sensor can be an important tool for timely protection of human being and environment.

Sensing odour is crucial to reduce health risk and avoid accidents. However, monitoring and measurements of odour is a difficult task due to low concentration. The sensor technology of artificial olfaction had its origins with the discovery of the first gas multisensory array in 1982 (Persaud and Dodd, 1982). Improvements in aroma-sensor technology, electronics and artificial intelligence made it possible to generate devices capable of measuring and characterizing volatile aromas released from a multitude of origins for various applications. These devices are known as an electronic nose. It recognizes the identification of a mixture of organic samples, and identifies individual's chemical species (Shurmer, 1990, Lonergan et al., 1996). A numbers of different prototypes of artificial nose devices have been developed to distinguish vapor mixture (Yea et al., 1994). Semiconductor gas sensor, optical sensor, electrochemical gas sensor, surface acoustic wave (SAW) is certain prototypes for electronic aroma detection (EAD) technology (Freund and Lewis,1995). Gas sensor has gained popularity due to its ability to detect hydrogen gas in fuel cells, methane in mining, hydrocarbons in refinery, nitrogen dioxide in automobile, ammonia in fertilizer industries (Sansone, 1992; Bhattacharyya et al., 2007; Wales, et al., 2015; Wetchakun et al., 2011; Ghosh et al., 2013). However, monitoring of pollutants causing odour are rare due to unavailability of reliable, real time and cost effective instrument or devices.

Metal oxide-based gas sensors may prove to be an ideal tool as it has excellent properties of ideal gas sensor (Hahn et al., 2003; Korotcenkov et al.,2004; Shouli et al., 2010). The ideal gas sensors show essential features such as fast response or recovery time, high sensitivity, low detection limit, long durability and wide operating temperatures.

Nanostructured material has attracted attention due to small size and large surface area, which may enhance gas-sensing properties. The sensing response of gas sensor depends upon the shape and size (dimension) of nanostructure (Liao, et al., 2007a,b; Choi & Jang, 2010). Nanostructure includes thin films, plates, needles, ribbons, wires, rods, flowers, tubes etc. Nanostructures can be prepared or synthesized by a number of methods such as chemical vapor deposition, sol-gel, radio frequency sputtering, hydrothermal, electro-spinning, molecular beam epitaxy, template synthesis, organic

chemical vapor deposition etc. Different types of structures can be obtained by using different methods of synthesis.

Chemical vapor deposition- Chemical vapor deposition (CVD) is a vacuum deposition method used to produce high quality, high-performance, solid materials. The process is often used in the semiconductor industry to produce thin films. The substrate is presented to one or more volatile precursors, which react and decompose on the substrate surface to produce the desired deposit. Generally, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

Sol-Gel - Sol-gel technique has been used for creating gas-sensitive films. The sol-gel process includes the formation of a solution (sol) and a colloidal suspension of solid particles. Then the solution is subjected to gelation (gel—where cross-linking between particles occurs), this can give a combination of new materials with other new properties. The solution then undergoes evaporation, giving a highly porous xerogel film.

Radio frequency sputtering - RF or Radio Frequency Sputtering is the technique involved in alternating the electrical potential of the current in the vacuum environment at radio frequencies to avoid a charge building up on certain types of sputtering target materials, which over time can result in arcing into the plasma that spews droplets creating quality control issues on the thin films – and can even lead to the complete cessation of the sputtering of atoms terminating the process.

Hydrothermal - The hydrothermal synthesis method involves using any one of the many techniques to crystallize substances. It usually does at a high vapor pressure level and using a high-temperature aqueous solution; hence it is termed as 'Hydro' + 'Thermal' = Hydrothermal method. Hydrothermal synthesis can be described as an artificial way to synthesize single-crystal (nanoparticles). It also depends on the solubility of the aqueous solution under hot water and higher temperature levels. A strong container is being kept within the hydrothermal reactor 'Autoclave,' and fills with a solution. The process much constant maintenance of temperature difference between the opposing ends of the crystallizing compartment.

Electro-spinning – Electro-spinning is a manufacturing technique involving electrostatic driven process used to create electro-spun fibers. The diameter of these fibers typically ranges between tens

of nanometers to a few micrometers. One of the main advantages of the electro-spinning technique is its versatility of processing to create fibers with multiple arrangements and morphological structures. The popularity of the electro-spinning technique has allowed multiple technologies such as tissue engineering, regenerative medicine, and encapsulation of bioactive molecules, to emerge and evolve over the past decade.

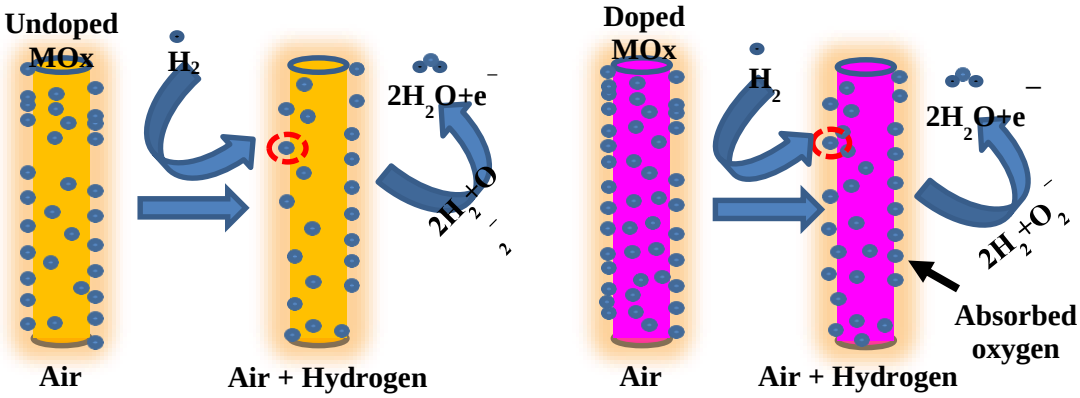
Molecular beam epitaxy - Molecular-beam epitaxy **(**MBE**)** is an epitaxy method for thin-film deposition of single crystals. MBE is widely used in the manufacture of semiconductor devices, including transistors, and it is considered as one of the fundamental tools for the development of nanotechnologies. Molecular-beam epitaxy is also used for the deposition of some types of organic semiconductors. In this case, molecules, rather than atoms, are evaporated and deposited onto the wafer. Other variations include gas-source MBE, which resembles chemical vapor deposition. MBE systems can also be modified according to need.

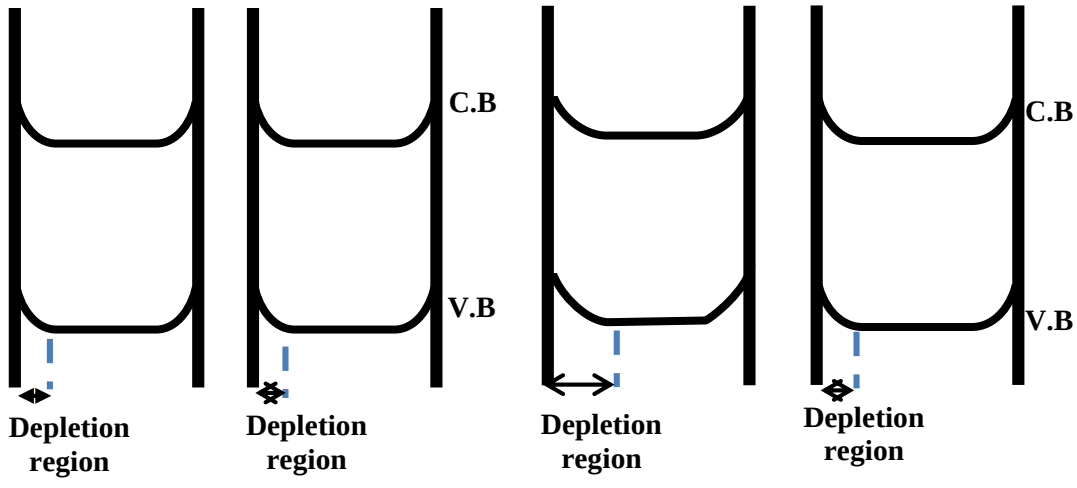
Template synthesis - Template synthesis is one of the most promising methods for the preparation of mono dispersed inorganic nanoparticles, in which the uniform void spaces of porous materials are used as hosts to confine the synthesized nanoparticles as guests. The role of the template is twofold. It allows the reproduction of the structure with the best possible reproducibility and plays the role of a skeleton to organize the different functions of a device, the active components, and the different interfaces.

Metal organic chemical vapor deposition (MOCVD) - MOCVD is a chemical vapor deposition method used to produce single or polycrystalline thin films. It is a process for growing crystalline layers to create complex semiconductor multilayer structures. In contrast to the molecular-beam epitaxy (MBE), the growth of crystals is by chemical reaction and not a physical deposition. This takes place not in vacuum, but from the gas phase at moderate pressures. This technique is preferred for the formation of devices incorporating thermodynamically metastable alloys, and it has become a major process in the manufacture of optoelectronics.

In metal oxide semiconductor-based gas sensors, sensors response is highly dependent on the surface of the metal oxide semiconductor (Shankar & Rayappan, 2015). Resistive gas sensors based on metal oxide such as SnO_2, NiO, CuO, WO_3 and ZnO are the usual attractive gas sensors because of their low

cost, easy operation, simple synthesis, and workability for miniaturization. Most commonly used metal oxide based semiconductors are n-type such as ZnO and SnO_2. These gas sensors are highly sensible for both reducing gases like H_2, H_2S, CO, ethanol etc. and oxidizing gases such as O_2, NO_2. LFO ($LaFeO_3$) based sensors have been reported for volatile organic compounds monitoring. Among the metal oxide, ZnO is a well-known n-type semiconductor shows the original characteristics required for an ideal gas sensor (Gupta et al., 2010). ZnO-based gas sensors are broadly employed in various applications due to their excellent sensing response, good selectivity, easy fabrication, non-toxicity, good thermal and chemical stability, low cost and ecofriendly. ZnO is a chemo resistive sensor. The change in its resistance depends upon the presence of chemisorbed oxygen ions. In the presence of atmospheric air, oxygen molecules are absorbed on the surface of ZnO. The reduction in resistance takes place when reducing gas interacts with chemisorbed oxygen ions.





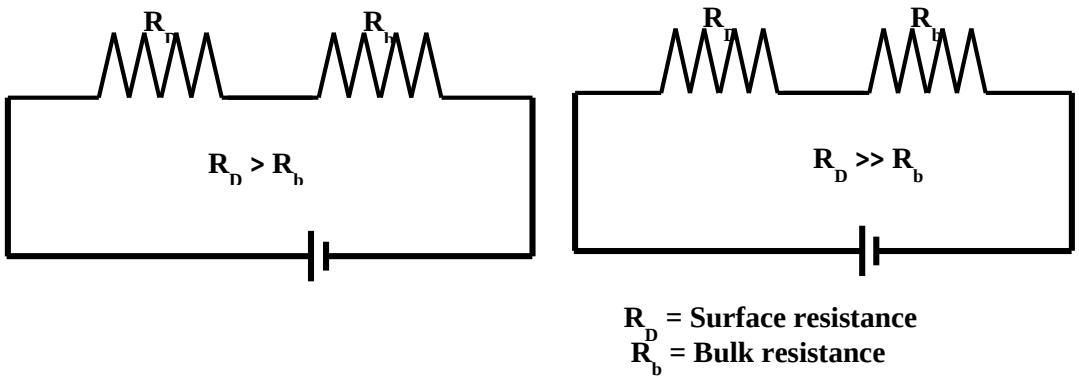


Fig. 1: Undoped and doped MOx nanorods and sensing mechanism.

Gas sensing mechanism of nanostructure based gas sensors relies on the alteration of a depletion layer on the surface of metal oxide nanostructures. The oxygen molecules are adsorbed on the MO surface in the presence of atmospheric air (Fig. 1). Furthermore, the formation of oxygen ions occurs on the surface due to the extraction of electrons from the conduction band of MO, leading to an increase in the resistance of MO. In other way, it can be also understood by band bending theory. The adsorption of oxygen ions on MO increases the band bending in upward direction under atmospheric oxygen due to high electronegativity of oxygen molecules and increased the barrier height (Dey, 2018). Moreover, the adsorbed oxygen ions (O_2^-, O^- and O^{2-}) are highly dependent on working temperature (Ranwa et al., 2014).

The sensing response can be improved by metal doping into MO_x, functionalization of noble metal nanoparticles on MO surface, inclusion of carbonaceous nanostructures, composition of different MO_x nanostructures, UV activation and e-beam irradiation

Doping - Doping to the metal oxide semiconductor with different metals like transition metal (Ni, Co, Cr, Fe), rare earth metal (Yb, Ce, La) and noble metal (Pd, Pt, Au) has been put great attention to enhance the sensing properties of gas sensors The main idea of doping is to increase the catalytic activity and changing the resistance of host metal oxide.

Functionalization of noble metal - The gas sensing response can be enhanced via the functionalization of noble metal nanoparticle on the surface of nanostructures. Two types of mechanisms are commonly used to describe the improved sensing response by functionalized noble

metal nanoparticles on nanostructures. The first one is chemical mechanism' and the second is electronic mechanism.

Composting - Highly sensitive and selective gas sensors can be made by using the combination of two different metal oxides (mixing of p- type to the n- type). The reason behind the mixing is to creating the heterojunction between the p- type and n- type metal oxide materials. The total resistance of the gas sensor becomes different and the sensitivity of the sensor shows maximum at the optimum concentration of p-type and n-type.

UV activation - The sensing response of nanostructures-based gas sensors relies on the adsorbed oxygen ions. The formation of this adsorbed oxygen (an ion) on the surface strongly depends on the working temperature. The use of sensors at high operating temperatures is recommended due to the possible modification in the sensor's morphology, high power consumption, and reduction of depletion layer on surface. Therefore, high sensing response, good selectivity, and fast response time should be achieved at either low operating temperature or room temperature

High energy irradiation- The irradiation sources include gamma-ray irradiation, ion beam irradiation, electron-beam irradiation, and laser irradiation, The physical and chemical properties of the sensor can be modulated using these sources. While irradiating the nanostructures, energy is released in the form of core-level ionization and generation of electron-hole pairs, however, irradiation induced modification of the structural properties of the sensor occurs due to the introduction of several defects, such as oxygen vacancies and interstitials. The sensing response of irradiation-induced the sensor is strongly dependent on irradiation dose and radiation energy.

Al doped ZnO (AZO) thin film is reported to exhibit low residual stress, high electron mobility and large crystallite size (Kumar et al., 2018). The gas sensing properties of ZnO has been improved by doping of metals into ZnO, functionalization of noble metal nanoparticles on the surface of ZnO, composting ZnO with other metal oxides, UV activation, high energy irradiation on ZnO nanostructures and inclusion of carbonaceous nanomaterial into ZnO (Bhati et al.,2018; Zhang, et al., 2018; Yang, et al., 2019; Kim et al., 2019).

2. REVIEW OF LITERATURE

Research work in generating an effective and reliable sensor film for the detection of odour has been going on all over the world. A literature survey has been carried out and summary of work done on development of thin films/sensor for monitoring of gases are presented here.

Marsal et al. (2003) developed a new material for CO_2 sensing based on resistive changes by utilizing hydrated $LaCl_3$ as the precursor and through two different synthesis routes simple oxidation and a sol–gel derived method. The undoped tin oxide showed a good response to CO_2 at 100 ºC. They examined sensing characteristic of these powders with special importance on their response to CO at a wide range of relative humidity and their cross-sensitivity with CO. They reported sensor response to CO_2 concentrations ranging from 500 to 5000 ppm.

Wang et al. (2006) developed the thin film from gold/Tin dioxide powder by deposition-precipitation method followed by calcination at 200ºC. The gold/tin dioxide was found to be efficient carbon monoxide gas sensing material between the low temperatures of 83-210ºC. The Au/ SnO_2 sensors with SnO_2 calcined at 300ºC exhibited better CO gas sensing behavior than the SnO_2 calcined at other temperatures.

Tischner et al. (2008) developed a thin film of SnO_2 by Spray pyrolysis method on a silicon substrate with a thickness between 50 and 100 nm on oxidized silicon substrate. The characterization of the sensor was done by SEM and AFM to determine the structure and morphology of SnO_2. The response of fabricated sensor film was tested against the humidity and CO. The sensor was able to detect the CO between the operating temperatures of 250ºC-400ºC.

Herran et al. (2009) investigated a thin-film technology of $BaTiO_3$-CuO (Barium-Titanate copper oxide) material for sensing carbon dioxide. The coating is deposited by RF-Sputtering and CO_2 concentration is monitored by impedance measurement. The $BaTiO_3$-CuO layers show higher sensitivity than the actual low-cost commercial CO_2 Sensors in the range of the main purpose.

Ghimbeu et al. (2010) investigated the electrostatic spray deposition of tungsten oxide (WO_3) films for the detection of different gaseous pollutants. The influence of several types of precursors on the structure and morphology of the films was studied utilizing X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The gas response to NO_2 and SO_2 is low at 150 ºC suggesting

no possible interference with these two gases during the H_2S detection. Furthermore, the films can detect very low concentrations of NO_2 (less than 1 ppm) at 150 ºC. Also, the films are highly sensitive to low H_2S concentrations (10 ppm) at low operating temperatures (200 ºC).

Yoon et al. (2011) reported high-performance graphene carbon dioxide (CO_2) gas sensors fabricated by mechanical cleavage. Unlike other solid-state gas sensors, the graphene sensors can be operated under ambient conditions and at room temperatures. Advances in the device conductor are measured for several concentrations of CO_2 gas (from 10 to 100 ppm). The response time of the sensor is less than 10 second suggesting that the device shows a fast response to CO_2 gas.

Manjula et al. (2011) developed tin oxide synthesized by the hydrothermal method and impregnated with Au for CO sensing in air at the room temperature. The response was very fast and stable for 1.5 wt. % at room temperature for 500 ppm CO gas.

Bancolo et al. (2012) studied SnO_2 nanomaterial fabricated by horizontal vapor phase growth technique. The nanostructures formed were deposited on a silicon substrate to test the sensitivity of the material in a carbon dioxide gas environment operated at room temperature. The growth temperature was the same for all the various dwell times at 1200ºC with a ramp rate of 10ºC/min. The surface topography, morphology and elemental composition of the synthesized SnO_2 nanomaterial were investigated using the SEM and EDX. They found nanostructure to be sensitive to CO_2 gas exposure.

Sarfraz et al. (2012) studied fabrication and demonstration of a low-cost PANI/$CuCl_2$ based H_2S sensor on paper substrates. Copper chloride films on paper substrates containing ink-jet printed silver electrodes have been prepared and are shown to be promising low-cost gas-sensors for H_2S at room temperature. These films showed large changes in conductivity (three to four orders of magnitude) upon exposure to low concentrations of H_2S (10 ppm). The response was comparable to the best reported for corresponding sensors on non-absorbing substrates using special PANI particle morphologies.

Nikan et al. (2013) explored effects of ZnO on response and selectivity of SnO_2 based sensor for CO. They fabricated ZnO-doped SnO_2 fibers and synthesized by electro spinning method and measured the sensitivity towards CO gas. The sensor responses were measured in presence of 300 ppm of CO in air at 200-400 ºC in a flow system. Even CO conversion versus temperature was studied for 1wt. % Zn

doped and SnO_2 and it was found that CO conversion needed relatively for low temperatures for pure tin oxide.

Hien et al. (2014) studied Tin Oxide (SnO) thin films. SnO of 100 nm in thickness, were deposited on glass substrates by RF magnetron sputtering. The NH_3 sensing properties of the SnO sensor at the operating temperature of 50-200ºC were examined, in which the p-type semiconducting sensing properties of the thin film were noted. The sensor shows good sensitivity and repeatability to NH_3 vapor.

Tyagi et al. (2014) developed SnO_2 thin film matrix integrated with nano-clusters of metal oxide. For low level (500 ppm) detection of SO_2 gas at a lower operating temperature of 180°C. Ultrathin dotted clusters (10 nm thick and 600 μm dia.) of various metal oxide catalysts (PdO, CuO, NiO, MgO, V_2O_5) were loaded over the SnO_2 surface. Due to the difference in the work function of the SnO_2 layer concerning the integrated metal oxide catalyst, all prepared sensor structures exhibited high resistance in the air. SnO_2 film with NiO nano-clusters is found to exhibit a maximum sensing response of ~56 at a low operating temperature of 180°C towards 500 ppm of SO_2 gas with a fast response time of 80 second.

Sonker et al. (2015) developed the thin film of ZnO, was fabricated on the surface of the corning glass substrate and Pt interdigital electrodes (IDEs) were grown over the thin film. This film was employed for NO_2 gas sensing at room temperature. The maximum sensing response 1.19 towards 20 ppm NO_2 gas with a fast response and recovery times of 1.42 and 1.71 min respectively was observed.

Yadav et al. (2015) stated that Zinc oxide (ZnO) is a very fascinating material due to its versatile application generated by various properties like wide band gap (3.37 eV), high excitation binding energy (60 meV) and hexagonal wurtzite structure. They prepared 0.075M intrinsic ZnO thin films at 330 ˚C core temperatures and low substrate temperature (220˚C) by using a modified spray CVD technique to sense H_2S gas. The structural investigation is done using XRD. The film surface and three-dimensional morphology are studied with FESEM and AFM, respectively. Pure ZnO thin film shows sensitivity S≈20% (S=Ra-Rg/Ra) to 10 ppm of H_2S gas at 300 ˚C operating temperature with fast response and recovery time.

Su et at. (2016) developed novel room temperature for NH_3 gas sensors based on Pd, tin oxide (SnO_2) and reduced graphene oxide (rGO) ternary Nano composite ($Pd/SnO_2/RGO$) film fabricated by the one-pot route. The $Pd/SnO_2/RGO$ ternary Nano composite films were characterized by Fourier transform infrared spectroscopy (FTIR), Raman, X-ray diffractometry (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The sensor that was based on a $Pd/SnO_2/RGO$ ternary Nano composite film responded strongly to low concentrations of NH_3 gas at room temperature.

Jiao et al. (2016) studied ZnO nanorods (NRs) selectively grown on a chip with a two-step low-temperature hydrothermal method and their gas sensing properties. Two-step with fresh precursor solution is needed to promote the majority of long NRs and thus to create NR junctions between small growth islands. Test with NO_2, ethanol, hydrogen, and ammonia showed that the gas sensor had a very high sensitivity of 6.1 to 10 ppm NO_2 at 450ºC and very high selectivity to NO_2 related to the contained gases.

Tyagi et al. (2016) investigated fabrication of SO_2 gas sensors using SnO_2 thin film integrated with various metal oxide catalysts (PdO, CuO, NiO, MgO, V_2O_5) in the form of 10 nm thin dotted clusters of 600μm diameter. The bare SnO_2 thin film sensor exhibits the sensing response of about 1.3 at 220°C whereas, NiO/SnO_2 sensor shows the enhanced sensing response (~56) towards 500 ppm SO_2 gas at a relatively low operating temperature (180°C). A correlation has been established between the observed sensing response and the properties of the sensing film. They tested selectivity of the NiO/SnO_2 sensor towards different interfering gases and found to be highly selective for SO_2 gas.

Tao et al. (2017) investigated Bi_2MoO_6 (Bismuth Molybdenum oxide) Nano sheet synthesized by a hydrothermal method. Morphology and structure of the Bi_2MoO_6 nanosheet were analyzed by SEM, XRD, N_2 absorption technique and XPS. Gas sensing properties of the prepared Bi_2MoO_6 sensors were also systematically investigated. During the reaction, the temperature reached 170ºC the morphology of the Bi_2MoO_6 Nano sheets tended to regular, and pure Bi_2MoO_6 Nano sheets were obtained. At this optimal operating temperature of the 300ºC, the sensitivity of the Bi_2MoO_6 sensors towards 20 ppm nitrogen oxide (NO) reached a maximum of 3.13. They reported that with the increase of the nitrogen oxide (NO) concentration, the selectivity of the Bi_2MoO_6 sensors also rapidly increased.

Chen et al. (2017) investigated SnO_2-nanorods coupled with reduced graphene oxide (rGO) nanostructures. They synthesized through a hydrothermal method, and studied their NH_3 sensing properties. The microstructure and morphology of the as-prepared materials were characterized by SEM, TEM, Raman spectroscopy, XPS, FT-IR spectroscopy and BET. A gas sensor fabricated from the as-prepared 3-D structure of SnO_2-nanorods coupled by rGO was investigated for the ammonia sensing properties. Most importantly, the sensor exhibited good sensitivity to NH_3 at room temperature. This sensor performed a fast response and recovery time for 200 ppm NH_3 at room temperature, which were 8 sec. and 13 sec., respectively.

Tyagi et al. (2017) investigated the radio-frequency sputtering technique to deposit tin (IV) oxide (SnO_2) thin films on platinum (Pt) interdigital electrode-patterned glass substrates for conductometric gas-sensing measurements. Various catalysts (zinc (Zn), indium (In), gold (Au), aluminum (Al)) in the form of circular patterns having a diameter of 600 mm have been deposited on the tin (IV) oxide surface. They monitored sensing response towards the target sulfur dioxide (SO_2) gas for these sensor structures (catalyst/tin (IV) oxide). They have done X-ray diffraction and ultraviolet-visible spectrophotometry studies to investigate its structural and optical properties.

Zhang et al. (2017) developed a sulfur dioxide (SO_2) gas sensor based on transition metal doped molybdenum disulfide (MoS_2) Nano composite synthesized via a facile single-step hydrothermal route. The Ni doped, Fe-doped, Co-doped and pristine MoS_2 film sensors were fabricated on FR4 epoxy substrate with interdigital electrodes (IDEs). The gas-sensing properties of the four samples were systematically investigated at room-temperature, and Ni-doped MoS_2 film sensor was screened out as the optimal SO_2 sensor among the four sensors, which exhibits relatively high response value, quick response/recovery time, and excellent stability toward SO_2 gas.

Wang et al. (2017) studied ZnO nanowire-reduced graphene oxide to detect ammonia at room temperature. The Nano composites are synthesized through the hybridization of ZnO nanowires and graphene oxide sheets, which have been produced on a large scale through mechanical mixing and low-temperature thermal reduction process. The micro ammonia sensors are subsequently constructed by the dip-dropping method. The resultant device exhibits excellent response (~19.2%) to NH_3 at room temperature, which is much better than pure reduced graphene oxide-based gas sensors.

Nimbalkar et al. (2019) developed Aluminum doped ZnO thin films have been synthesized by using a sol-gel spin coating method. They studied effect of Al-doping on physicochemical and NO_2 sensing properties of the AZO thin films. The structural and compositional analysis confirms the phase formation of ZnO and the substitution of aluminum atoms into zinc oxide lattice. The NO_2 sensing study reveals that the 2 at% AZO film sensor shows excellent gas sensing characteristics at 200 °C.

He et al. (2019) investigated a highly sensitive H_2S gas sensor based on WO_3/ CuO composite. They selected CuO nanoparticles to modify the surface of the flower-like WO_3 by two-step hydrothermal methods. The morphology and structure of the samples were examined by XRD, SEM, TEM, and BET. They examined sensing properties of the samples on H_2S at different operating temperatures, and also investigated the performance of WO_3/CuO with different molar ratios. The sensitivity of the WO_3/CuO composite with a 7:1 M ratio to 5 ppm H_2S gas reached 105.2 at an optimized operating temperature of 80ºC, and the response time was 42 s. At the same time, WO_3/CuO composite-based sensor is even able to receive a high response of 16 to 5 ppm H_2S at room temperature (28ºC).

3. Objectives

Environmental pollutants and general odour are two main hurdles faced by humankind in these days in our country. Air quality has been degrading worldwide and particularly in developing countries and posing extinction threats. Besides the industrial/vehicular/domestic sources, solid waste and its decomposition has also increased the levels of different types of pollutants in the air. Some of the outdoor and indoor air pollutants cause foul odour and constitute a variety of compounds viz., hydrogen sulphide, mercaptans volatile organic carbons (VOCs) like benzene, acetone, methanol, formaldehyde etc. Some of these gases are carcinogenic in nature also. Volatile organic compounds are toxic and vulnerable to many unwanted diseases. The leakage of some of the gases may be fatal to human safety and environment. Real time measurements and detections may avoid accidents and casualty. However, due to costly instruments and non-availability of suitable and reliable sensors or devices, a limited study has been carried out on monitoring and characterization of odour and odour causing species. Hence, there is a need to develop a low cost, environment friendly and portable indigenous gas sensors/devices for monitoring of odour.

With this in view the aim of the present investigation is:

- To synthesize thin film for detection of odour and odour causing pollutants,
- To characterize synthesized thin film material using SEM-EDS and AFM (for shape, size, surface roughness and arrangement of constituent particles), XRD (for phase analysis and particle size), and different spectrometer techniques to find the band gap etc. and
- To measure and enhance the efficiency of developed gas sensor.

4. Material and methods:

4.1 Preparation of thin films: Thin films will be prepared to fabricate the gas sensors for monitoring and measurements of odour/pollutants in the environment. Desired nanostructure will be obtained by growing nanomaterial using the Sol-Gel/Spray pyrolysis/RF magnetron sputtering. 1-D nanostructure (Nanorods, nanotubes, nanowires etc.) based gas sensor is one of the promising technology because of its high surface to volume ratio and miniaturization capability that helps in achieving low temperature gas sensing, enhance sensitivity and stability. The doping of transition metal element will be added into the host metal oxide semiconductors such as ZnO and SnO_2 and subsequently, their sputtering target will be made.

4.2 Material characterization: The structural and morphological characterization of nanomaterial will be carried out using SEM, EDX, FESEM, XRD and Raman Spectroscopy. The morphological (size, shape, and surface) study will be performed using SEM. X-Ray diffraction technique will be used for structural and phase analysis. Size of the particle would be determined using Scherrer equation ($0.9\lambda/\beta\cos\theta$). The thickness of the film will be determined by using surface profilometer. Band gap will be determined by plotting $(\alpha\lambda\gamma)^{1/2}$ versus $h\upsilon$ using the equation $\alpha = A(h\upsilon - Eg)^{1/2}$. UV-Visible Spectrometer will be used to obtain absorption data.

4.3 Fabrication of sensors

Doping: Doping to the metal oxide (SnO_2 and ZnO) semiconductor with different metals like transition metal (Ni, Co, Cr, Fe), rare earth metal (Yb, Ce, La) and noble metal (Pd, Pt, Au) has attracted great attention to enhance the sensing properties of gas sensors. The doping to the metal oxide semiconductor will be done to increase the catalytic activity and changing the resistance of host metal oxide. The dopants will be distributed uniformly throughout the host metal oxide matrix. Oxygen ions are formed on interaction of oxygen molecule to these dopants and then spill over on the

entire metal oxide surface during exposure to air. On exposure of target gas to the metal oxide, oxygen ions reacts and resulting to a large change in the conductivity as well as sensitivity. Enhancement in sensitivity is due to the reduction in grain, which correspondingly increases the surface area. The gas sensing, electronic and chemical properties of doped metal oxide semiconductor become quite different as compared to pure metal oxide semiconductor.

4.4 Combination of nanomaterial: The highly sensitive and selective gas sensors will be made by using the combination of two different metal oxides (mixing of p- type to the n- type). Heterojunction will be formed between the p-type and n-type metal oxide material. The total resistance of the gas sensor becomes different and the sensitivity of the sensor shows maximum at the optimum concentration of p-type and n-type. These structures are known as the hybrid nanostructures.

4.5 Decoration of nanomaterial on metal oxide: The sensitivity of gas sensor will be enhanced by decoration of nanomaterial on metal oxide semiconductor. The optimum concentration of nanomaterial will be decorated on interdigitated electrodes (IDE)/metal oxide. The nature of these nanomaterial would be opposite (if metal oxide is n- type then decorated material should be p –type or vice versa). Schottky barrier height will be increased which will enhance the sensitivity of any gas sensor towards a particular gas. The decoration of nanomaterial will be processed using drop cast method as it is simple and easy to use.

Usually, the gold (Au) based interdigitated electrode (IDE) is widely used for fabricating the gas sensors because of large Schottky barrier height that is beneficial for excellent sensing. The electrode deposition process on sensing layer will be done by optical lithography or using thermal evaporator. Therefore, the sensing studies on these fabricated materials will be performed with the desired concentrations (extremely low concentrations~1-20 ppm) of toxic species as well as VOCs.

4.6 Sensing measurement

The gas sensing characterization of sensors will be done in a customized gas sensing chamber. The gas sensing characterization will be carried out for a range of concentration at optimized operating temperature. The eveloped sensor will be used for monitoring hydrogen sulphide and VOCs. The data will be collected, analyzed and compared with data obtained through other methods or instruments.

5. Expected Outcome

This research will help in enhancing the understanding of existing knowledge in the area of gas sensing as well as help in reducing the chances of accidents and improve the safety of human and environment. The metal oxide based gas sensor with high sensitivity will be prepared for monitoring of odour and measurements of odour causing environmental pollutants. Electrodes will be patterned by lithography and activation energy will be provided by using low power LEDs. Selectivity and sensitivity will be enhanced by using the adsorption layers, plasmonic, controlling the grain size and Schottky contacts. The developed sensor will be of low cost, highly sensitive and robust.

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